12

BAND SPECTRUM OF MERCURY BROMIDE IN THE ULTRAVIOLET REGION

M. M. PATEL AND A. B. DARJI

DEPARTMENT OF PHYSICS, FACULTY OF SCIENCE,
M. S. UNIVERSITY OF BARODA, BARODA, INDIA.

(*Received September* 16, 1966; *Resubmitted January* 20, 1968)

(Plate 4)

ABSTRACT. The band spectrum of mercury bromide in the ultraviolet region has been excited in high frequency discharge and photographed in the first and second order of a plane grating spectrograph having a dispersion of 3.5 and 1.85 A°/mm. respectively. The bands in the region λλ 2900 to 2760 Å have been analysed into a single system which forms one of the components of the electronic transition $^2\Pi \rightarrow {}^2\Sigma$ with a $^2\Pi$ interval of 3852 cm^{-1}. Another group of bands reported earlier by Krishnamurthy in the region λλ 2770 to 2700 Å has been analysed and designated as due to a transition $^2\Sigma \rightarrow {}^2\Sigma$. New vibrational constants of these systems have been evaluated.

INTRODUCTION

Spectroscopic studies on the band spectrum of mercury bromide has been carried out by Wieland (1929, 1932, 1939, 1960), Sastry (1941), Howell (1943) and Krishnamurthy (1958). The vibrational analysis of the violet degraded bands in the region λλ2670 to 2430 Å was made by Wieland and the system was assigned to a transition $^2\Pi \rightarrow {}^2\Sigma$. The origin of the system was located at 38574 cm^{-1}. The longer wavelength end of the spectrum was first considered by him to be due to a polyatomic molecule because of its complexity but it is now realised that this is unlikely. The strongest bands were at 34580 and 34668 cm^{-1}. It has been suggested by Howell (1943) that if one of these is the first member of the $\Delta v = 0$ sequence of the other component of $^2\Pi \rightarrow {}^2\Sigma$ transition, one obtains a doublet separation of either 3996 or 3906 cm^{-1}, and both these values are in excellent agreement with the values for HgF and HgCl. In the later work of Krishnamurthy (1958) however, existence of another system has been suggested with a $^2\Pi$ interval of 969.4 cm^{-1}. In view of these discrepancies it was thought desirable to re-investigate the spectrum and the results obtained are reported here.

EXPERIMENTAL

The spectrum of mercury bromide was excited in high frequency discharge from a 125 Watt oscillator working in the frequency range of 10-15 M.c./sec. A pure sample of the substance was kept in the cavity of a conventional type of

Indian Journal of Physics
Vol. 42 No. 2
PLATE - 4

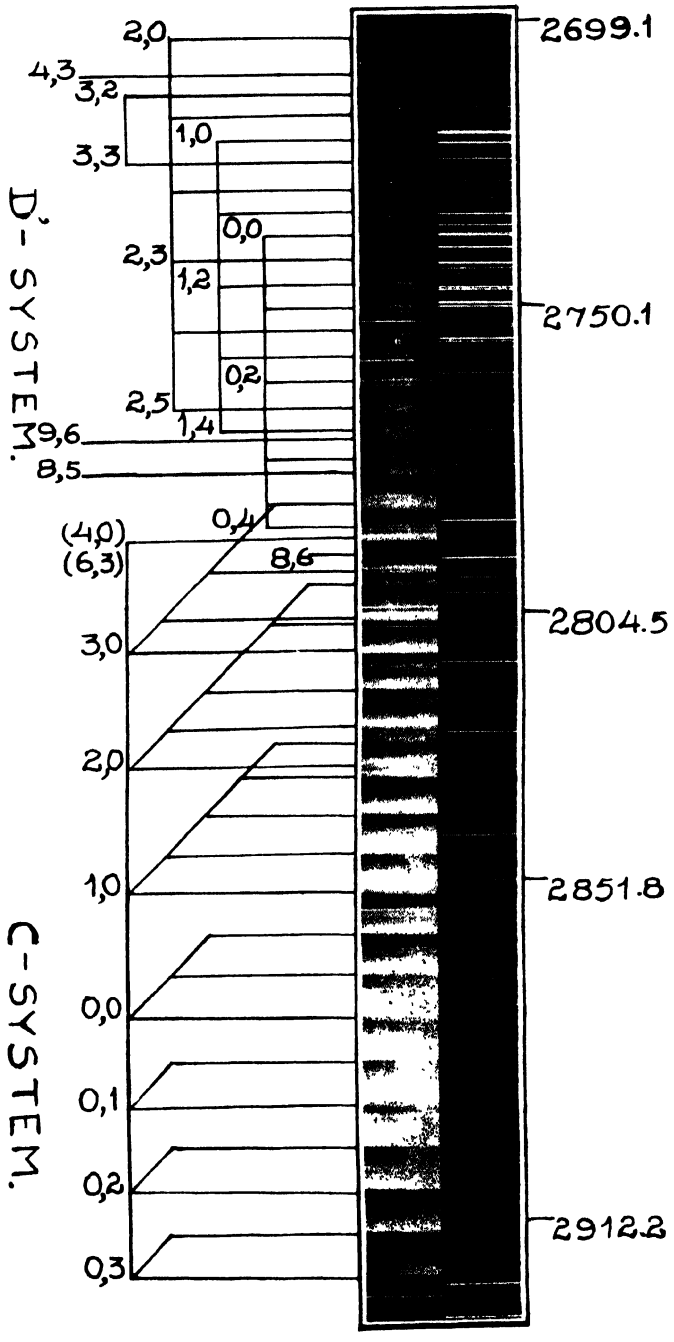

Fig. 1 The band spectrum of HgBr molecule in the region λλ 2935-2699A° taken with plane grating spectrograph in the second order double passage.

pyrex discharge tube. The discharge was established by external electrodes and was maintained bright green in colour only by occasional heating. Continuous evacuation of the discharge tube with a high vacuum pump was necessary. Photographs of the spectra were taken with a plane grating spectrograph (Carl Zeiss Jena) in the first and second order with double passage thereby getting a dispersion of 3.5 and 1.85 Å/mm respectively. An exposure of about 45 minutes was found adequate to record the spectrum on Ilford process plates. Iron arc lines were used as standards for determining the wavelengths.

RESULTS

The spectrum of mercury bromide in the region $\lambda\lambda$2935—2699 Å has been reproduced in fig. 1 (Plate 4). The bands are degraded towards the violet. Those on the longer wavelength side are sharp and show some structure but those on the shorter wave length side are diffuse and most of them have double heads. In tables 1 and 2, corresponding to C and D' system, wave lengths, wave numbers in vacuum, assignments and visiually estimated intensities of the bands obtained in the present investigation are given. In the last column the wave numbers of the bands re- ported by Krishnamurthy are given for comparison. The calculated isotopic shifts along with the observed isotopic shifts for about twenty four bands of the of the C-system have been given in table 4.

A list of additional bands of the D-system previously analysed by Wieland, has been given in table 3 along with the assignments based on his analysis.

DISCUSSION

As reproduced in fig.1., the bands in the region $\lambda\lambda$2912 to 2850 Å are very intense and the (0, 0) band may lie in this region. As proposed by Krishnamurthy, the (0, 0) band is taken at 34767.6 cm^{-1} and the analysis is extended further. Unlike that reported by Krishanurthy, the regularity of intervals is fairly good if the isotopic shifts of bands having higher quantum numbers are taken into consideration. Further, there is no justification to select the bands at 35738.2 and 35557.8 cm^{-1} respectively as (0, 0) and (0, 1) bands of the other sub-system proposed by him. This has happened probably because of the poor resolution in the spectrum recorded by the previous worker. In the present study the band at 35738.2 cm^{-1} shows two components at 35739.1 and 35747.6 cm^{-1} and these are assigned as the isotopic heads of (5, 2) band. In the same way the band at 35557.8 cm^{-1} has been resolved into two components at 35557.5 and 35565.8 cm^{-1} and these are assigned as the isotopic heads of (5, 3) band. From the plate it is clear that the bands in the longer wavelength region ($\lambda\lambda$2968—2770 Å) are having an altogether different appearance from those below λ2790 Å and as suggested by the previous worker the former group of bands may belong to a $^2\Pi \rightarrow {}^2\Sigma$ transition. The later group shows clear double headed nature and in all probability belongs

Table 1

Positions of band heads, visiually estimated intensities and quantum classification numbers of the *C*-system of mercury bromide in the region $\lambda\lambda$2968—2766 Å

Intensity	Wave length A° λ	Wave number in vacuum ν cm.$^{-1}$	Assignment	Value Observed by Krishnamurthy ν cm.$^{-1}$
0	2968.64	33675.6	0,6(79)	
1	2967.91	33683.9	0,6(81)	
2	2953.67	33846.3	0,5(79)	
3	2952.68	33857.7	0,5(81)	
2	2944.04	33957.0	1,6(79)	
2	2943.55	33962.8	1,6(81)	
6	2937.59	34031.6	0,4	
0	2936.17	34048.0	2,7(79)	
0	2935.71	34053.4	2,7(81)	
4	2928.96	34131.8	1,5(79)	34126.7
4	2928.37	34138.7	1,5(81)	
7	2921.83	24214.7	0,3(79)	34215.7
8	2921.41	24220.0	0,3(81)	
4	2914.14	34305.4	1,4(79)	34307.1
5	2913.53	34310.4	1,4(81)	
8	2906.38	34397.0	0,2(79)	34398.0
9	2906.14	34399.8	0,2(81)	
6	2898.80	34487.0	1,3	34487.0
7	2890.91	34581.0	0,1	34582.4
8	2883.26	34672.9	1,2	34670.0
3	2875.87	34761.9	2,3	
10	2875.39	34767.6	0,0	34768.8
6	2868.00	34857.3	1,1	34857.3
4	2861.01	34942.7	2,2	34942.6
2	2853.42	35035.4	3,3	35038.1
9	2852.94	35041.3	1,0 (81)	35040.6

Table 1 (*Contd.*)

Intensity	Wave length A° λ	Wave number in vacuum ν cm.$^{-1}$	Assignment	Value Observed by Krishnamurthy cm^{-1}
9	2852.57	35045.8	1,0 (79)	
8	2846.36	35122.3	2,1	35120.6
6	2839.28	35210.0	3,2 (81)	35202.2
7	2838.82	35215.6	3,2 (79)	
4	2833.10	35286.7	4,3 (81)	35280.4
4	2832.56	35293.4	4,3 (79)	
6	2831.06	35312.2	2,0	35310.3
5	2827.29	35359.2	5,4 (81)	35359.7
5	2826.74	35366.0	5,4 (79)	
4	2824.72	35391.4	3,1 (81)	35391.6
5	2824.05	35399.7	3,1 (79)	
3	2819.53	35456.9	6,5 (81)	35444.3
3	2818.92	35464.2	6, 5 (79)	
5	2817.87	35477.4	4,2 (81)	35477.0
5	2817.37	35483.5	4,2 (79)	
6	2811.52	35557.5	5,3 (81)	35557.8
6	2810.87	35565.8	5,3 (79)	
6	2809.50	35583.2	3,0 (81)	
7	2808.71	35593.3	3,0 (79)	
5	2805.76	35630.5	6,4	35630.0
5	2804.22	35650.0	4,1	
4	2799.10	35715.3	7,5	35708.9
2	2797.28	35739.1	5,2 (81)	35738.2
3	2796.57	35747.6	5,2(79)	
2	2793.82	35782.0	8,6	35774.1
6	2792.40	35800.0	(6,3), (4,0) (81)	
6	2791.74	35809.6	(6,3), (4,0) (79)	35809.9
4	2786.11	35881.8	7,4(81)	35879.3
4	2785.31	35892.0	7,4 (79)	

Table 1 (*Contd.*)

Intensity	Wave length A° λ	Wave number in vacuum ν cm.$^{-1}$	Assignment	Value Observed by Krishnamurthy cm.$^{-1}$
3	2783.50	35915.4	5,1 (81)	
3	2782.99	35922.0	5,1 (79)	
1	2780.00	35960.0	8,5 (81)	35955.5
1	2779.30	35969.8	8,5 (79)	
2	2774.65	36030.0	9,6 (81)	36029.3
2	2773.91	36039.0	9,6 (79)	
1	2766.83	36131.8	8,4 (81)	
1	2765.85	36148.5	8,4 (79)	

Table 2

Position of the band heads their visually estimated intensities and quantum classification numbers of the D'-system of mercury bromide in the region λλ2789-2694 Å

Intensity	Wave length A° λ	Wave number in Vacuum ν cm^{-1}	Assignment	Value observed by Krishnamurthy ν cm^{-1}
4	2789.63	35836.5	0,4	35835.6
4	2788.51	35850.9	0,4	
5	2777.24	35996.3	0,3	35990.4
5	2776.33	36008.0	0,3	36002.1
4	2772.39	36059.3	1,4	
4	2771.36	36072.7	1,4	
5	2768.95	36104.1	2,5	36106.1
5	2767.54	36122.5	2,5	36119.8
9	2763.76	36171.9	0,2	36166.1
9	2762.59	36187.0	0,2	36180.6
8	2759.70	36225.1	1,3	36223.8

Table 2 (*Contd.*)

Intensity	Wave length A°	Wave number in Vaccum ν cm^{-}	Assignment	Value observed by Krishnamurthy
7	2758.59	36239.7	1,3	36238.3
6	2755.70	36277.7	2,4	36277.7
6	2754.74	36290.3	2,4	36292.2
10	2751.34	36335.2	0,1	36335.7
9	2750.30	36348.9	0,1	36350.3
10	2747.04	36392.1	1,2	36391.3
9	2745.74	36409.3	1,2	36405.9
10	2742.77	36448.6	2,3	36451.0
9	2741.60	36464.3	2,3	36465.6
8	2738.05	36506.6	0,0	36506.6
7	2737.39	36520.4	0,0	36520.4
7	2734.33	36561.2	1,1	36560.3
6	2733.27	36575.4	1,1	36575.0
4	2730.06	36618.4	2,2	36613.9
3	2728.81	36635.0	2,2	36628.6
3	2727.30	36655.5	3,3	
2	2726.37	36668.1	3,3	
4	2720.45	36747.8	1,0	
3	2719.44	36761.4	1,0	
2	2716.66	36799.0	2,1	
2	2715.53	36814.3	2,1	
3	2714.04	36834.5	3,2	
3	2712.44	36856.3	3,2	
2	2703.76	36974.6	2,0	
2	2702.42	36992.9	2,0	
2	2695.60	37086.5	5,3	
2	2694.30	37104.4	5,3	

Table 3

Positions of the additional band heads, visually estimated intensities and quantum classification numbers of the *D*-system of mercury bromide in the region $\lambda\lambda 2710-2668$ Å

Intensity	Wave number in Vacuum ν cm^{-1}	Assignment
1	36894.2	1,11 (79)
1	36905.4	1,11 (81)
1	36950.8	2,12 (79)
1	36967.0	2,12 (81)
1	37053.3	1,10 (79)
2	37067.0	1,10 (81)
2	37124.5	2,11 (81)
2	37162.9	0, 8 (79)
2	37175.2	0, 8 (81)
3	37226.3	1, 9 (79)
3	37233.6	1, 9 (81)
2	37284.3	2,10 (79)
2	37295.4	2,10 (81)
3	37334.0	0, 7 (79)
3	37348.4	0, 7 (81)
3	37392.4	1, 8 (79)
3	37410.9	1, 8 (81)
2	37450.2	2, 9 (79)
2	37460.4	2, 9 (81)

Table 4

Isotopic shifts of some of the bands of the *C*-system of mercury bromide in the region λλ2968—2766 Å

Assignment v', v''	Δν obs. cm^{-1}	Δν cal cm^{-1}
0,6	− 8.3	− 9.6
0,5	−11.4	− 7.9
1,6	− 5.8	− 7.1
2,7	− 5.4	− 6.3
1,5	− 6.9	− 5.4
0,3	− 5.3	− 4.6
1,4	− 5.0	− 3.8
0,2	− 2.8	− 2.9
1,0	4.5	2.9
3,2	5.6	4.5
4,3	6.7	5.3
5,4	6.8	6.1
3,1	8.3	6.2
6,5	7.3	7.0
4,2	6.1	7.0
5,3	8.3	7.8
3,0	10.1	7.8
5,2	8.5	9.5
6,3	9.4	10.3
7,4	10.2	11.1
5,1	7.4	11.1
8,5	9.2	11.9
9,6	9.0	12.7
8,4	16.7	13.6

to a $^2\Sigma \rightarrow {}^2\Sigma$ transition. An almost constant separation of about 15 cm^{-1} is observed for all the bands of this system. Theoretical considerations also indicate a possibility of a $^2\Sigma$ state of nearly the same energy as that of the $^2\Pi$ state. It is therefore reasonable to assign this system a transition $^2\Sigma \rightarrow {}^2\Sigma$.

The band at 35836 cm^{-1} has been resolved into four components. Amongst them the two on the longer wavelength side are more intense than the other two and they may belong to the $^2\Pi \rightarrow {}^2\Sigma$ system. The band may be assigned as either (6, 3) or (4, 0) as the calculated isotopic shifts for both of them are nearly equal. However, the regularity of intervals is better when it is arranged in the vibrational scheme as (6, 3) instead of (4, 0). The two less intense bands on the shorter wavelength side will belong to $^2\Sigma \rightarrow {}^2\Sigma$ system and the observed separation of 14.4 cm^{-1} (table 2) between them is in good agreement with an almost constant separation of 15 cm^{-1} observed for the bands of $^2\Sigma \rightarrow {}^2\Sigma$ system.

In the present analysis it is observed that the lower state frequencies for both the systems are almost the same and are also equal to the lower state frequency of the farther ultra-violet system which occurs in the region $\lambda\lambda 2665$ to 2470 Å. In the present study the $^2\pi$ interval between C and D systems comes out to be 3852 cm^{-1} and is in good agreement with that proposed by Howell. Since bromine has two isotopes Br^{79} and Br^{81} having an abundance ratio of 50.57: 49.43, one may expect the intensities of the corresponding bands to be nearly the same. The isotopic shifts have been calculated for the bands of the C-system and the agreement between observed and calculated shifts is fairly close (Table 4), while the isotopic shifts for the bands of D'-system are not of appriciable magnitude. The following quantum equations represent the observed band heads of the two systems (long wavelength components for D'-system).

C-system. $\nu_{head} = 34722.04 + [278.64(v'+\frac{1}{2}) - 1.82(v'+\frac{1}{2})^2]$

$(^2\Pi \rightarrow {}^2\Sigma)$ $\quad - [187.29(v''+\frac{1}{2}) - 0.96(v''+\frac{1}{2})^2]$

D'—system. $\nu_{\substack{head \\ (long\ \lambda\ comp.)}} = 36482.05 + [233.80(v'+\frac{1}{2}) - 1.68(v'+\frac{1}{2})^2]$

$(^2\Sigma \rightarrow {}^2\Sigma)$ $\quad - [184.50(v''+\frac{1}{2}) - 1.15(v''+\frac{1}{2})^2]$

The observed and calculated values of the wave numbers are in fairly good agreement (± 3 cm^{-1}) for the bands of the C-system while the deviations are slightly more in the case of the D' system.

ACKNOWLEDGMENT

The authors are grateful to Prof. N. S. Pandya for his keen interest in the work. One of the authors (A.B.D.) is grateful to Government of Gujarat for financial assistance.

REFERENCES

Howell H. G., 1943, *Proc. Roy. Soc. Lond.*, **182**, 95-112.
Krishnamurthy, V. G., 1958, *Z. Fur. Physik*, **152**, 242.
Sastry, M. G., 1941, *Proc. Nat. Inst. Sc. India*, **7**, 359.
Wieland K., 1929, *Helv. Phys. Acta.*, **2**, 46 and 77.
1932, *Z. Fur, Physik.*, **77**, 157.
1939, *Helv. Phys. Acta.*, **12**, 295.
1960, *Z. Electrochem*, **64**, 761.